

Solubility and Size Separation of Large Fullerenes in Concentrated Sulfuric Acids[†]

Pradeep K. Rai,^{‡,§} A. Nicholas G. Parra-Vasquez,^{‡,§} Haiqing Peng,[‡] Robert H. Hauge,^{‡,||} and Matteo Pasquali^{*,‡,§,||}

Carbon Nanotechnology Laboratory, Smalley Institute for Nanoscale Science and Technology, and Department of Chemical and Biomolecular Engineering, MS-362, and Department of Chemistry, MS-60, Rice University, 6100 Main Street, Houston, Texas 77005

Received: March 28, 2007; In Final Form: June 22, 2007

We show that large fullerenes (LFs) are soluble in concentrated sulfuric acids. We employ a centrifugation technique in conjunction with ultraviolet–visible and near-infrared (UV–vis–nIR) spectroscopy to quantify solubility. The Beer's Law dependence of UV–vis–nIR absorbance of LFs in concentrated sulfuric acids between 400 and 1400 nm facilitates the construction of linear calibration curves for measuring LF concentration in acids. Centrifugation of concentrated dispersions of LFs in concentrated sulfuric acids results in a clear phase separation. UV–vis–nIR absorbance measurements on the less concentrated phase yield the solubility of LFs. Large fullerenes exhibit an unusually high solubility in sulfuric acids concentrated in the range of 88–96%. The solubility of LFs in 96% sulfuric acid is higher than the solubility of the smallest fullerene (C₆₀) in many organic solvents. We find that the solubility of LFs grows with acid strength, as is expected for solubilization by a protonation mechanism. Moreover, the average size of LFs solubilized in sulfuric acid increases with the strength of the acid.

1. Introduction

Since the discovery of fullerenes by Smalley and co-workers,¹ the physical and chemical properties of C₆₀ and C₇₀ fullerenes have been widely investigated. Fullerenes represent a unique category of cage molecules with a wide range of sizes, shapes, and molecular weights.² The potential for applications in material sciences^{3,4} such as superconductors,^{5,6} batteries, catalysts, or novel optical devices,^{7,8} or in organic or pharmaceutical chemistry^{9–13} is enhanced by the possibility of producing fullerenes of different sizes and shapes. Besides the relatively well-known C₆₀ and C₇₀ fullerenes, a large class of so-called “fullerene” compounds such as nanotubes¹⁴ or onion-like nanostructures¹⁵ have been identified and investigated. Fullerene chemistry continues to be an exciting field; many articles are published every year with advances in basic science and promising applications.^{16,17}

2. Methods and Discussion

Fullerenes have limited solubility in common solvents. Ruoff and co-workers¹⁸ investigated the temperature-dependent solubility of C₆₀ in hexane and toluene; comprehensive lists of solubility of C₆₀ in various solvents can be found in refs 19–21 and references therein. Fullerenes themselves are virtually insoluble in water;²² potential applications in biology and medicine have motivated attempts to make water-stable systems. Limited water solubility of fullerenes has been achieved by chemical modification,^{20,23–26} formation of water-soluble host–guest complexes,^{27,28} or solubilization by surfactants.^{28–29} Specifically, C₆₀ fullerene has been made soluble by connecting

it with functional chargeable groups such as carboxylic acids,^{30–32} amines^{33,34} or phenyl groups.^{35–37} Deguchi et al.³⁸ reported stable aqueous dispersions of C₆₀ and C₇₀ prepared by injecting a saturated solution of fullerene in tetrahydrofuran (THF) into water, followed by THF removal by purging with gaseous nitrogen.

Though smaller fullerenes, such as C₆₀, C₇₀, C₇₆, and C₈₄, have been widely studied, less is known about the characterization and processing of large fullerenes (LFs, >C₁₀₀). Most studies on LFs are concentrated on molecular mechanics calculations of shape, size, and geometry,^{39–42} and electronic structure.^{43,44} Macroscopic characterization by IR, Raman, nuclear magnetic resonance (NMR), X-ray diffraction (XRD), and transmission electron microscopy (TEM) is rarely reported⁴⁵ as are the identification and extraction of LFs.^{46–48}

The studies most relevant to the work described here are those of Cataldo⁴⁹ and Reed et al.,⁵⁰ who report stabilization of fullerenes through the use of superacids. Cataldo⁴⁹ report that oleum oxidizes C₆₀ with free SO₃, leading to the formation of C₆₀ cations. Chiang and co-workers^{51–53} have also reported polycyclosulfation of C₆₀ with fuming sulfuric acid (28–30 wt % excess SO₃). Similar findings are also reported by Kukulich and Huffman.⁵⁴ Reed et al.⁵⁰ report reaction of the superacid H(CB₁₁H₆X₆) (where X = chlorine or bromine) with C₆₀ to give HC₆₀⁺ as a stable ion in solution and in the solid state. The protonation of C₆₀ is reversible. Exposure of the solution to a base via aerobic moisture or by the addition of Na₂CO₃(s) returns the spectrum to that of C₆₀. To the best of our knowledge, however, the solubility of LFs in any solvent has never been reported. Here, we report the unusually high solubility of LFs in concentrated sulfuric acids (64–96% H₂SO₄) and a convenient route to separate LFs by size.

Our technique for quantifying the solubility of LFs in concentrated sulfuric acids relies on centrifugation in conjunction with a method for measuring the concentration of dispersions

[†] Part of the special issue “Richard E. Smalley Memorial Issue”.

^{*} To whom correspondence should be addressed. E-mail: mp@rice.edu.

[‡] Carbon Nanotechnology Laboratory, Smalley Institute for Nanoscale Science and Technology, Rice University.

[§] Department of Chemical and Biomolecular Engineering, Rice University.

^{||} Department of Chemistry, Rice University.

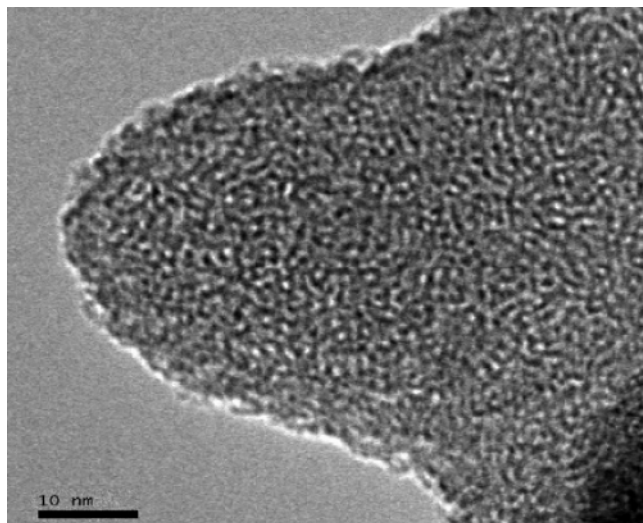


Figure 1. TEM image of the starting material showing large fullerenes.

of LFs in acids by UV–vis–nIR spectroscopy.⁵⁵ A higher-order fullerene mixture was acquired from the Materials and Electrochemical Research (MER) Corporation (Tucson, Arizona). Smaller fullerenes (C_{60} and C_{70}) were removed from this mixture by dissolving them in ortho-dichlorobenzene, because the ortho-dichlorobenzene has one of the highest solubilities for C_{60} .²² A matrix-assisted laser desorption ionization (MALDI) mass spectrum proves that this material is fullerene (see Figure 4a and also Supporting Information). The raw sample shows a mass spectral span of 1200–4500 amu with the maximal intensity at 1850 amu. The masses were evenly separated at a spacing of 24 amu, a well-known feature in the mass spectral pattern of fullerenes arising from the loss of C_2 species.^{56,57} The MALDI spectrum also shows the absence of small fullerenes such as C_{60} or C_{70} in the starting material. Figure 1 is a TEM image of the starting material showing that it consists of mostly LFs. Lighter fullerenes such as C_{60} or C_{70} and carbon nanotubes are present in very small quantities in the starting material, if at all. Thermogravimetric analysis (TGA) shows that metal content of the sample is less than 2 wt %. ACS-certified 96% sulfuric acid was purchased from Sigma Aldrich and was used as received without purification. Lower concentrations of sulfuric acid were prepared by slowly adding water to 96% sulfuric acid and mixing with a magnetic stirrer. LF dispersions were prepared by gentle mixing with a magnetic stir bar (no sonication) for a minimum of 72 h at room temperature in an anhydrous environment (a glovebox with a dewpoint of -50 °C) to prevent moisture ingress. After mixing, the samples were centrifuged on a Fisher Centrifugal model 225 benchtop centrifuge at 5100 rpm. UV–vis–nIR absorbance spectra were measured on a Shimadzu UV-3101PC spectrometer in 1 mm path-length Starna cells with Teflon closures. Elemental analysis of dissolved LFs was performed by X-ray photoelectron spectroscopy (XPS) on a PHI Quantera XPS.

At low concentrations of LFs in sulfuric acids, light absorbance in the range from 400 to 1400 nm scales linearly with concentration. This Beer's Law behavior yields calibration curves for measuring LFs concentration in acids. Concentrated dispersions of LFs in concentrated sulfuric acids were centrifuged for 12 or more hours (after which no measurable changes in concentration could be detected in the centrifugation vials); phase separation was visible in the lower acidity samples. The lower absorbance of the fullerene dispersion in the dilute phase at all wavelengths shows that phase separation occurs during the process of centrifugation. The less concentrated phase was

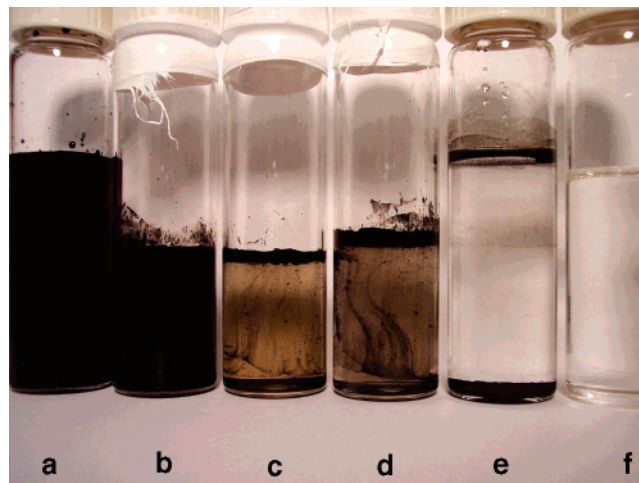


Figure 2. Photographic image of large fullerenes centrifuged in different strengths of sulfuric acid showing the extent and trend of phase separation. Large fullerenes centrifuged in (a) 96% H_2SO_4 , (b) 88% H_2SO_4 , (c) 84% H_2SO_4 , (d) 80% H_2SO_4 , and (e) 64% H_2SO_4 . (f) Pure 96% H_2SO_4 is shown here for comparison.

diluted with a known amount of solvent; UV–vis–nIR absorbance measurements provided a quantitative measurement of concentration.

Figure 2 shows photographs of vials of LFs centrifuged from a starting concentration of 1500 ppm (or 0.15 wt %) in different strengths of sulfuric acid ((a) 96%, (b) 88%, (c) 84%, (d) 80%, and (e) 64%); these dispersions display various extents of phase separation upon extended centrifugation at 5100 rpm. A vial of 96% H_2SO_4 (Figure 2f, shown for comparison) is a clear liquid. The phase separation of LFs from 64% H_2SO_4 is almost complete; therefore, the solubility of LFs in 64% sulfuric acid is minimal. In 64% H_2SO_4 ($\rho_{64\%} = 1.44$, $\rho_F = 1.65$; where $\rho_{64\%}$ is the density of the 64% sulfuric acid and ρ_F is the density of the LFs) the top phase is structureless and optically uniform, whereas the bottom phase includes most of the fullerenes. In 80–84% sulfuric acid ($\rho_{80\%} = 1.73$ and $\rho_{84\%} = 1.77$), where the density of the fullerenes is only slightly lower than that of the solvent, phase separation of fullerenes is visible upon centrifugation; most of the LFs cream at the top. However, the acid has acquired some coloration, indicating that some of the LFs have dissolved. Some particles are visible in the dilute phase. These are due to the minimal difference in density between LFs and 80–84% sulfuric acid; removing the vials from the centrifuge causes some of the top to diffuse. In 88% H_2SO_4 ($\rho_{88\%} = 1.80$), the initial dispersion of LFs, upon centrifugation, separates into a low concentration supernatant solution and a concentrated flocculated suspension of fullerenes in acid at the bottom. This phase separation is not obvious in the photographic image in Figure 2 because of the high solubility of LFs in 88% H_2SO_4 , but it is clear from microscopic observation and UV–vis–nIR measurements. It is surprising that the LF-rich phase would be at the top in 80–84% sulfuric acid and at the bottom in 88% acid because the density of the acid grows with SO_3 content. This behavior is similar to that of single-walled carbon nanotubes in sulfuric acids,^{55,58} where the protonated nanotubes associate with ordered sulfuric acid into a higher-density mixture.⁵⁹ In 96% H_2SO_4 ($\rho = 1.84$), the dispersion is fully stable, and no phase separation occurs over 48 h of continuous centrifugation. On the basis of the analysis of Holladay⁶⁰ and the relative densities of LFs and 96% sulfuric acid, we estimate that particles above ~ 5 nm would separate under the centrifugation conditions. This suggests that, in 96% H_2SO_4 , the LFs are present as individuals (i.e., their solubility is higher than 1500

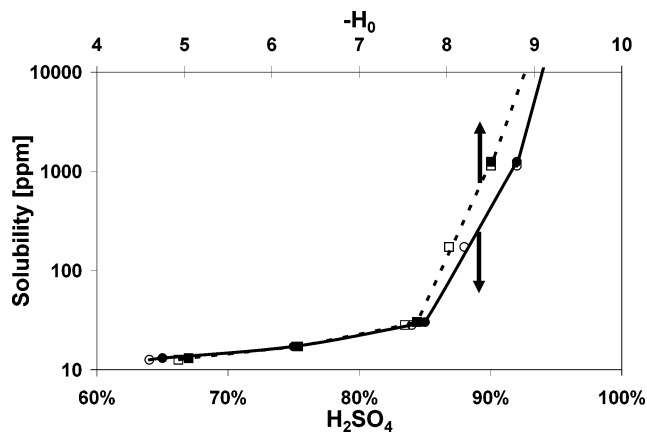


Figure 3. Solubility of large fullerenes versus H_2SO_4 concentration (circles) and versus Hammett acidity (H_0 , squares). The open and closed symbols are from two different data sets. The solubility of large fullerenes is higher than 10 000 ppm in 96% H_2SO_4 .

ppm). A similar experiment with 10 000 ppm (1 wt %) LFs in 96% sulfuric acid showed that, within experimental uncertainty (about 3%), no phase separation occurred upon centrifugation. Therefore, the solubility of LFs in 96% H_2SO_4 is above 10 000 ppm (or 18 mg/mL). By comparison, the solubility of buckyballs (the smallest fullerenes) is less than 5 mg/mL in most organic solvents.²² Of all the one-ring aromatic solvents, ortho-dichlorobenzene has the highest solubility for C_{60} ; the solubility approaches that achieved with naphthalene derivatives. The solubility of C_{60} in 1,2-dichlorobenzene is 27 mg/mL, and in 1-chloronaphthalene it is 51 mg/mL.^{20,22}

Figure 3 shows the solubility of LFs versus H_2SO_4 concentration and Hammett acidity. The Hammett acidity factor values used in this plot are according to Paul and Long.⁶¹ Because the solubility of LFs is higher than 10 000 ppm in 96% H_2SO_4 , it does not appear in this plot. Remarkably, the solubility of LFs rises sharply when the sulfuric acid concentration exceeds 85%, corresponding to a Hammett acidity of 7.5. It is worth remarking that at the 84.5% concentration of sulfuric acid the molar ratio of H_2SO_4 and H_2O in the solution is 1:1 (i.e., $84.5/98 = 15.5/18$) at which point there are only bisulfate (HSO_4^-) and hydronium (H_3O^+) ions in the medium. Only above this concentration the moles of H_2SO_4 exceed the moles of H_2O in solution, and free H_2SO_4 molecules are present in the solution. Free H_2SO_4 molecules undergo auto-ionization according to $2\text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{SO}_4^+ + \text{HSO}_4^-$. The free H_3SO_4^+ radical can protonate fullerenes (in the absence of competition from free water molecules) and stabilize fullerenes. The overall reaction of fullerenes with H_2SO_4 can be represented as $\text{fullerene} + \text{H}_2\text{SO}_4 \rightarrow \text{fullerene}^+ + \text{HSO}_4^-$, which, of course, can occur only at acid concentrations above 84.5%. This is reflected in the enhanced solubility data of the fullerenes above 84–85% H_2SO_4 , corroborating earlier observations (on single-walled carbon nanotubes) that fullerenes are being stabilized and solubilized by protonation. This particular transition in the molar ratios of H_2SO_4 and H_2O is not captured by the Hammett acidity function, which varies almost linearly over the range of acid strength of interest here; nevertheless, the Hammett acidity function is also included in the Figure 3 because it is a thermodynamic measure of the proton accepting/donating ability of a solvent system.

It is important to differentiate solubility from the formation of soluble functionalized complexes. Chiang and co-workers^{51–53} have reported polycyclosulfation of C_{60} with neat fuming sulfuric acid (28–30 wt %, excess SO_3) at 55–60 °C in an inert environment. In fuming sulfuric acid, the highly reactive

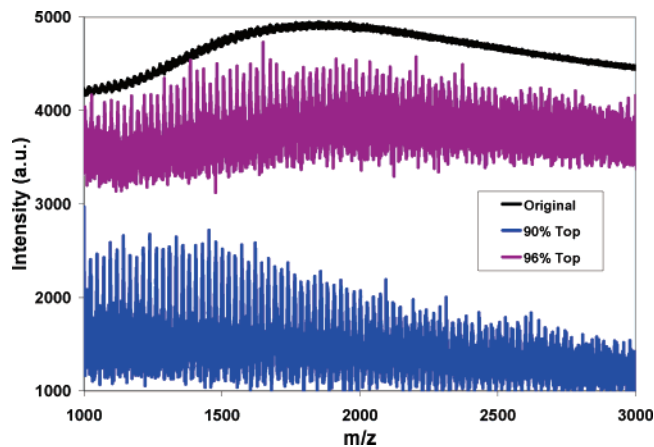


Figure 4. MALDI spectra of large fullerenes showing distribution of masses. The masses are evenly separated at a spacing of 24 amu, a well-known feature in the mass spectral pattern of fullerenes arising from the spacing of C_2 species. The size of the solubilized fullerenes grows with the strength of the H_2SO_4 .

sulfur trioxide first attacks the fullerenes.⁵¹ Similar findings are also reported by Kukolich and Huffman.⁵⁴ Polycyclosulfated fullerenes are reported to precipitate out from the acid solution as orange-red solids.⁵² Because our acid dispersion of LFs had neither SO_3 nor any solid precipitation, we believe that LFs are not functionalized but are truly soluble in concentrated sulfuric acids. We further checked that LFs are not functionalized by performing XPS. XPS identifies elements from lithium to uranium, with detection levels down to one atomic percent. If LFs are really functionalized in 96% sulfuric acid, then the XPS spectra should detect sulfur atoms. LFs were dissolved in 96% H_2SO_4 for two weeks and were subsequently quenched in ether and washed with methanol on a polycarbonate filter paper. The XPS spectra of these LFs (see Supporting Information) shows that the sample consists entirely of carbon atoms; the sulfur content is less than 0.1% (atomic), which is below the sensitivity of the instrument. This proves that LFs were not functionalized in concentrated sulfuric acids. We hypothesize that 96% H_2SO_4 is a strong enough acid to form a reversible polycarbonation similar to what is observed in the case of single-walled carbon nanotubes in fuming sulfuric acid.⁶² Such fractional charge on the carbon atoms is sufficient to stabilize the LFs but is not strong enough to functionalize them. Interestingly, no metal was detected in the XPS spectra.

The size distribution of LFs solubilized in different strengths of sulfuric acid was measured by MALDI spectroscopy. Because acid-stabilized dispersions of fullerenes do not show any MALDI peaks characteristic of fullerenes, it was necessary to transfer fullerenes from acid into an organic solvent.

Acid dispersions of fullerenes were quenched in nanopure water (15:1 excess water), soaked overnight, settled at the bottom of the vial by centrifuging for few minutes (~5 min), resuspended in nanopure water at least twice (to remove any residual acid), and then collected again at the bottom of the vial by centrifugation. Figure 4 shows the size distribution of LFs in the starting material and in those dissolved in sulfuric acid after quenching and washing with water. The mass spectra of the starting material shows the maximum intensity at 1850 amu. The mass spectra of LFs solubilized in 90% H_2SO_4 show the maximum intensity around 1450 amu and in 96% H_2SO_4 around 1700 amu, close to the starting material. This indicates that smaller LFs are solubilized preferentially in the weaker acids. This dependence of the size of solubilized LFs on the strength of sulfuric acid is consistent with the observation that even stronger acids (superacids) are needed to solubilize single-

walled carbon nanotubes.^{55,62,63} The ability to separate LFs by size by varying the strength of the acid provides an important advancement that could be useful in various applications.

3. Conclusion

A centrifugation technique has been used in conjunction with UV-vis-nIR spectroscopy to quantify the solubility of large fullerenes in concentrated sulfuric acids (weaker than 96% H₂SO₄). Large fullerenes exhibit an unusually high solubility in the range of 88–96% H₂SO₄. The solubility of large fullerenes is higher than 10 000 ppm, or 1 wt %, in 96% H₂SO₄. Large fullerenes are not functionalized in these concentrated sulfuric acids; therefore, the dispersion mechanism is dissolution. The average size of LFs solubilized in sulfuric acid increases with the strength of the acid. This work opens the way to further understanding the mechanism of large fullerene stabilization in acid dispersions, which will be important for the extraction, isolation, and purification of large fullerenes.

Acknowledgment. This article is dedicated to the memory of Professor Richard E. Smalley, who has contributed so much to the discovery, science, and applications of fullerenes and carbon nanotubes. We acknowledge the help of Sachin Khapli, Sandy Yates, Robert Pinnick, Howard Schmidt, W. Ed Billups, Lon Wilson, Donal Soward, and James Tour. Financial support was provided by the Advanced Technology Program of the state of Texas under Grant No. 003604-0113-2003 and by the DURINT initiative of the Office of Naval Research under Grant No. N00014-01-1-0789.

Supporting Information Available: MALDI spectra of large fullerenes in the starting material and XPS spectra of large fullerenes dissolve in 96% sulfuric acid for two weeks and then quenched in ether and washed with methanol. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
- (2) Dresselhaus, M. S. *Ann. Rev. Mater. Sci.* **1997**, *27*, 1.
- (3) Baum, R. M. *Chem. Eng. News* **1993**, *71*, 8.
- (4) Huffman, D. R. *Mater. Lett.* **1994**, *21*, 127.
- (5) Allemand, P.-M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Grüner, G.; Thompson, J. D. *Science* **1991**, *253*, 301.
- (6) Crespi, V. H. *Nat. Mater.* **2003**, *2*, 650.
- (7) Henari, F. Z.; Cazzini, K. H.; Weldon, D. N.; Blau, W. J. *Appl. Phys. Lett.* **1996**, *68*, 619.
- (8) Cravino, A.; Sariciftci, N. S. *Nat. Mater.* **2003**, *2*, 360–361.
- (9) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685.
- (10) Friedman, S. H.; DeCamp, D. L.; Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506.
- (11) Sijbesma, R.; Srdanov, G.; Wudl, F.; Castoro, J. A.; Wilkins, C.; Friedman, S. H.; DeCamp, D. L.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6510.
- (12) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317.
- (13) Tegos, G.; Demidova, T.; Arcilla-Lopez, D.; Lee, H.; Wharton, T.; Gali, H.; Hamblin, M. *Chem. Bio.* **2005**, *12*, 1127.
- (14) Iijima, S. *Nature* **1991**, *354*, 56.
- (15) Ugarte, D. *Carbon* **1995**, *33*, 989.
- (16) Hwang, K. C.; Mauzerall, D. *Nature* **1993**, *361*, 138.
- (17) Chhowalla, M.; Amaratunga, G. A. J. *Nature* **2000**, *407*, 164.
- (18) Ruoff, R. S.; Malhotra, R.; Huestis, D. L.; Tse, D. S.; Lorents, D. C. *Nature* **1993**, *362*, 140.
- (19) Marcus, Y.; Smith, A. L.; Korobov, M. V.; Mirakyan, A. L.; Avramenko, N. V.; Stukalin, E. B. *J. Phys. Chem. B* **2001**, *105*, 2499.
- (20) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807.
- (21) Herbst, M. H.; Dias, G. H. M.; Magalhaes, J. G.; Torres, R. B.; Volpe, P. L. O. *J. Mol. Liq.* **2005**, *118*, 9.
- (22) Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, *97*, 3379–3383.
- (23) Tabata, Y.; Murakami, Y.; Ikada, Y. *Jpn. J. Cancer Res.* **1997**, *88*, 1108–1116.
- (24) Okamura, H.; Ide, N.; Minoda, M.; Komatsu, K.; Fukuda, T. *Macromolecules* **1998**, *31*, 1859.
- (25) (a) Cerar, J.; Skerjanc, J. *J. Phys. Chem. B* **1998**, *102*, 7377. (b) Cerar, J.; Skerjanc, J. *J. Phys. Chem. B* **2000**, *104*, 727. (c) Cerar, J.; Skerjanc, J. *J. Phys. Chem. B* **2003**, *107*, 8255.
- (26) Samal, S.; Choi, B. J.; Geckeler, K. E. *Chem. Comm.* **2000**, *15*, 1373.
- (27) Jenekhe, S. A.; Chen, X. L. *Science* **1998**, *279*, 1903.
- (28) Lai, D. T.; Neumann, M. A.; Matsumoto, M.; Sunamoto, J. *Chem. Lett.* **2000**, *1*, 64.
- (29) Guldi, D. M. *J. Phys. Chem. A* **1997**, *101*, 3895.
- (30) Tokuyama, H.; Yamago, S.; Nakamura, E.; Shiraki, T.; Sugiura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7918.
- (31) Nakamura, E.; Tokuyama, H.; Yamago, S.; Shiraki, T.; Sugiura, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2143.
- (32) An, Y. Z.; Chen, C. H. B.; Anderson, J. L.; Sigman, D. S.; Foote, C. S.; Rubin, Y. *Tetrahedron* **1996**, *52*, 5179.
- (33) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850.
- (34) Murakami, H.; Shirakusa, M.; Sagara, T.; Nakashima, N. *Chem. Lett.* **1999**, *8*, 815.
- (35) Sawamura, M.; Iikura, H.; Hirai, A.; Nakamura, E. *J. Am. Chem. Soc.* **1998**, *120*, 8285.
- (36) Sawamura, M.; Toganoh, M.; Kuninobu, Y.; Kato, S.; Nakamura, E. *Chem. Lett.* **2000**, *3*, 270.
- (37) Zhou, S.; Burger, C.; Chu, B.; Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E. *Science* **2001**, *291*, 1944.
- (38) Deguchi, S.; Alargova, R. G.; Tsujii, K. *Langmuir* **2001**, *17*, 6013.
- (39) Adams, G. B.; Sankey, O. F.; Page, J. B.; O'Keeffe, M.; Drabold, D. A. *Science* **1991**, *256*, 1792.
- (40) Yoshida, M.; Osawa, E. *Fullerene Sci. Tech.* **1993**, *1*, 55.
- (41) Ugarte, D. *Europhys. Lett.* **1993**, *22*, 45.
- (42) Cai, W. S.; Xu, L.; Shao, N.; Shao, X. G.; Guo, Q. X. *J. Chem. Phys.* **2005**, *122*, 184318.
- (43) Dunlap, B. I.; Brenner, D. W.; Mintmire, J. W.; Mowrey, R. C.; White, C. T. *J. Phys. Chem.* **1991**, *95*, 8737.
- (44) Drabold, D. A.; Ordejon, P.; Dong, J. J.; Martin, R. M. *Solid State Commun.* **1995**, *96*, 833.
- (45) Selvan, R.; Unnikrishnan, R.; Ganapathy, S.; Pradeep, T. *Chem. Phys. Lett.* **2000**, *316*, 205.
- (46) Shinohara, H.; Sato, H.; Saito, Y.; Takayama, M.; Izuoka, A.; Sugawara, T. *J. Phys. Chem. B* **1991**, *95*, 8449.
- (47) Ramesh, S.; Brinson, B.; Johnson, M. P.; Gu, A.; Saini, R. K.; Willis, P.; Marriott, T.; Billups, W. E.; Margrave, J. L.; Hauge, R. H.; Smalley, R. E. *J. Phys. Chem. B* **2003**, *107*, 1360.
- (48) Sadana, A. K.; Liang, F.; Brinson, B.; Arepalli, S.; Farhat, S.; Hauge, R. H.; Smalley, R. E.; Billups, W. E. *J. Phys. B* **2005**, *109*, 4416.
- (49) Cataldo, F. *Spectrochim. Acta* **1995**, *51A*, 405.
- (50) Reed, C. A.; Kim, K.-C.; Bolskar, R. D.; Mueller, L. J. *Science* **2000**, *289*, 101.
- (51) Chiang, L. Y.; Wang, L.-Y.; Swirczewski, J. W.; Solde, S.; Cameron, S. *J. Org. Chem.* **1994**, *59*, 3960.
- (52) Chen, B.-H.; Huang, J.-P.; Wang, L. Y.; Shiea, J.; Chen, T.-L.; Chiang, L. Y. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1171–1173.
- (53) Chen, B.-H.; Canteenwala, T.; Patil, S.; Chiang, L. Y. *Synth. Comm.* **2001**, *31*, 1659.
- (54) Kukolic, S. G.; Huffman, D. R. *Chem. Phys. Lett.* **1991**, *182*, 263.
- (55) Rai, P. K.; Pinnick, R. A.; Parra-Vasquez, A. N. G.; Davis, V. A.; Schmidt, H. K.; Hauge, R. H.; Smalley, R. E.; Pasquali, M. *J. Am. Chem. Soc.* **2006**, *128*, 591.
- (56) O'Brien, S. C.; Heath, J. R.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* **1988**, *88*, 220.
- (57) Ulmer, G.; Campbell, E. E. B.; Kuhnle, R.; Busmann, H. G.; Hertel, I. V. *Chem. Phys. Lett.* **1991**, *182*, 114.
- (58) Ericson, L. M.; Fan, H.; Peng, H.; Davis, V. A.; Zhou, W.; Sulpizio, J.; Wang, Y.; Booker, R.; Vavro, J.; Guthy, C.; Parra-Vasquez, A. N. G.; Kim, M. J.; Ramesh, S.; Saini, R. K.; Kittrell, C.; Lavin, G.; Schmidt, H. K.; Adams, W. W.; Billups, W. E.; Pasquali, M.; Hwang, W.-F.; Hauge, R. H.; Fischer, J. E.; Smalley, R. E. *Science* **2004**, *305*, 1447.
- (59) Zhou, W.; Heiney, P. A.; Fan, H.; Smalley, R. E.; Fischer, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 1640.
- (60) Holladay, L. A. *Biophys. Chem.* **1979**, *10*, 187.
- (61) Table 3 of Paul, M. A.; Long, F. A. *Chem. Rev.* **1957**, *57*, 1.
- (62) Ramesh, S.; Ericson, L. M.; Davis, V. A.; Saini, R. K.; Kittrell, C.; Pasquali, M.; Billups, W. E.; Adams, W. W.; Hauge, R. H.; Smalley, R. E. *J. Phys. Chem. B* **2004**, *108*, 8794.
- (63) Davis, V. A.; Ericson, L. M.; Parra-Vasquez, A. N. G.; Fan, H.; Wang, Y.; Prieto, V.; Longoria, J. A.; Ramesh, S.; Saini, R. K.; Kittrell, C.; Billups, W. E.; Adams, W. W.; Hauge, R. H.; Smalley, R. E.; Pasquali, M. *Macromolecules* **2004**, *37*, 154.